Raman Scattering:- when electro-magnetic radiation of energy irradiates a molecule, the energy may be transmitted absorbed or scattered. In the Tyndall effect radiation is scattered by smoke or fog particles. In Rayleigh scattering the molecules scatter the light. No change in wavelength of individual photon occurs in either Tyndall or Rayleigh scattering. In 1920 C.V. Raman described another type of scattering called as Raman effect or Raman scattering. This had been theratically predicted by Smekal before the successful experimental demonstration by Raman and therefore sometimes it is referred as Smekal-Raman scattering in German literature.

In the Raman spectrometer, sample is irradiated with intense source of monochromatic radiation usually is visible part of spectrum. Generally this radiation frequency is much higher than vibrational frequencies but less

than electronic frequencies. The Raman scattering Can be looked as an inelastic ~~scattering~~ Collission between incident ~~and~~ photon and molecule as a result of this the vibrational or rotational energy of molecule is changed by an amount ΔE_m such that

$$\Delta E_m = E_i - E_s$$
$$= h\nu_i - h\nu_s$$

$\nu_i \rightarrow$ Incident frequency

$\nu_s \rightarrow$ Scattered frequency

If ΔE_m is positive, means ν_s is smaller than ν_i giving rise to Stokes Raman line

If ΔE_m is negative, means ν_s is greater than ν_i giving rise to antistokes Raman line.

The Raman scattering process can be described by

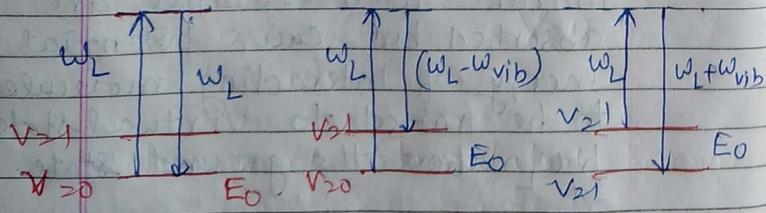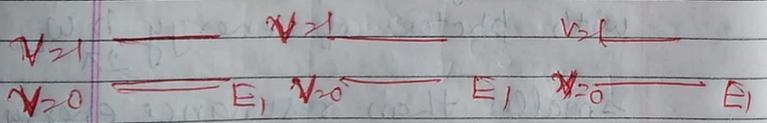$$P = \overset{(1)}{\chi} E + \overset{(2)}{\chi} E^2 + \overset{(3)}{\chi} E^3$$

In this equation, first term is connected with linear polarization describes spontaneous linear Raman scattering which is studied by Raman spectroscopy. The second and third term describe spontaneous nonlinear Raman scattering also called Hyper Raman scattering. The third term is also responsible for stimulated Raman scattering. The levels denoted as E_0 and E_1 represent electronic energy levels while the levels numbered with quantum number V vibrational levels. If sample is illuminated with photons of energy $\frac{h\omega_L}{2\pi}$

Smaller than resonance energy $\Delta E = E_1 - E_0$, not all photons interact with sample are absorbed but cause potential energy of interacting molecules to be raised to virtual state $\frac{h\omega_L}{2\pi}$ above the ground state.

Almost immediately, most

molecules return to the ground state through the emission of photons having same energy as the incident photons. This elastic Scattering is known as Rayleigh Scattering.

A small fraction of molecules drop back to first excited vibrational state ($V=1$) instead to ground state. In this case scattering is inelastic and process is known as Stokes Raman scattering. The scattered radiation observed at lower energy $\frac{h}{2\pi}(\omega_L - \omega_{vib})$.

$V=1$ _____ $V=1$ _____ $V=1$ _____

$V=0$ ===== E_1 $V=0$ ===== E_1 $V=0$ ===== E_1

ω_L ↑↓ ω_L ω_L ↑ $(\omega_L - \omega_{vib})$ ↓ ω_L ↑ $\omega_L + \omega_{vib}$ ↓

$V=1$ $V=1$ ↓ $V=1$

$V=0$ --- E_0 $V=0$ --- E_0 $V=1$ --- E_0

Rayleigh Scatt.   Stokes Raman   Antistokes
       Sca   Raman

Molecules that are already in excited state ($V=1$) will undergo an analogus effect when illuminated with laser light. When excited molecules drop back to ground vibrational state ($V=0$), the ~~scattering scattering~~ Scattered radiation will he observed at higher energy $\frac{h}{2\pi}(\omega_L + \omega_{vib})$

This is called antistokes Raman Scattering.

$\omega_{vib} \rightarrow$ Frequency of given vibrational mode of molecule

Stimulated Raman Scattering :-

Stimulated Raman scattering or Stimulated Raman Spectroscopy (SRS) was discovered by Woodbury and Ng in 1962. In their experiment, they introduced a cell containing Nitrobenzene into Ruby laser cavity. This resulted with strong emission at a wavelength

that could not be associated with wavelength of Ruby laser. At first this was explained on the basis of luminescence but after some years later Garmier explained it on the basis of two wave mixing. SRS is third order non linear optical phenomena. The mechanism of SRS is shown in figure
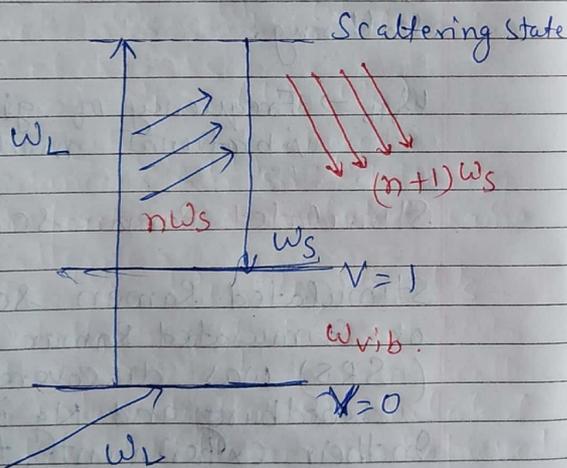
Schemes of Stimulated Raman Scattering

When incident light exceeds a certain threshold in the material, it can enhance or stimulate the rate of Raman Stokes or antistokes emission. This SRS shows a similarity to stimulated emission in the optically pump laser. The intense incident beam at frequency ω_L generates the intense Stokes radiation at the frequency

$$\omega_S = \omega_L - \omega_{vib}$$

The Stokes radiation, in turn stimulates additional Stokes scattering from the virtual scattering state. In constr contrast to linear Raman scattering the SRS can achieve 50% or more conversion of the pump wavelength to the Stokes line.

The stimulated Raman Scattering (SRS) is special case of four wave interaction

$$\omega_4 = \omega_1 + \omega_2 \pm \omega_3$$

$$\Delta K = K_1 + K_2 \neq K_3 - K_4 = 0$$

These equations describe a non degenerate case with four photons of different frequencies. The SRS represents a partially degenerate case $(\omega_1 = \omega_3, \omega_2 = \omega_4)$

The Stimulated Stokes scattering can be written in

$$\omega_4 = \omega_S = \omega_L - \omega_{vib}$$

$$= \omega_L - (\omega_L - \omega_S)$$

$$= \omega_L + \omega_S - \omega_L$$

therefore

$$\omega_4 = \omega_S, \quad \omega_1 = \omega_L, \quad \omega_2 = \omega_S$$

$$\omega_3 = \omega_L$$

The intensity of Stimulated Stokes Scattering is expressed as

$$\frac{I_S^{SRS}}{S} = Const \left[\chi^{(3)}\right]^2 I_L^2 I_S^a \ell^2 \left(\frac{\sin\frac{\Delta K \ell}{2}}{\frac{\Delta K \ell}{2}}\right)^2$$

In this $\chi^{(3)}$ denotes the effective susceptibility of third order.

For Stimulated antistokes scatt.

$$\omega_{AS} = \omega_L + \omega_{vib} = \omega_L + (\omega_L - \omega_S)$$

Therefore

$$\omega_4 = \omega_{AS}$$
$$\omega_1 = \omega_L$$
$$\omega_2 = \omega_L, \quad \omega_3 = \omega_S$$

Phase matching condition for Stimulated Stokes Scatt.

$$\Delta K = K_L + K_S - K_L - K_S = 0$$

which indicates that phase matching between pumping beam ω_L the Stokes beam ω_S and molecular vibrations is established automatically.
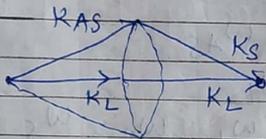
In the case of antistokes Stimulated scattering

$$\delta K = K_L + K_L - K_S - K_{AS}$$

$$= 2K_L - K_S - K_{AS}$$

This indicates that phase matching condition is achieved only for certain directions for which

$$K_{AS} = 2K_L - K_S.$$

Directions of stimulated anti Stokes SRS.

Comparison between Spontaneous Raman Scattering and SRS (Stimulated Raman Scattering)

The difference between spontaneous and stimulated Raman Scattering are as follows

(1) The intensity of spontaneous RS is several powers of ten lower than pumping while the intensity of stimulated RS is comparable with pumping Beam Intensity.

2. The stimulated RS is observed exclusively above the threshold intensities. The threshold depends on medium gain $g(\omega_S)$ and length of pumping area. The gain is expressed by

$$g(\omega_S) \propto \left(\frac{\partial \sigma}{\partial \Omega}\right)\left[\frac{\Gamma}{\left(\omega_L - \omega_S - \omega_{vib}\right)^2 + \Gamma^2}\right]$$

Here $\frac{\partial \sigma}{\partial \Omega} \rightarrow$ Scattering cross section

Γ = width of vibrational line

3. The spectral widths of spontaneous and stimulated Raman lines depend on spectral line width of pumping laser. For narrow widths of excitation lasers the stimulated Raman lines are much narrower than spontaneous Raman lines.

Schematic Representation of experimental set up used by Woodbury and Ng for observation of stimulated RS

M_1 $\lambda|4$ Laser Head   S M_2 L   SP

Pc   Polarizer   Sample   Lens
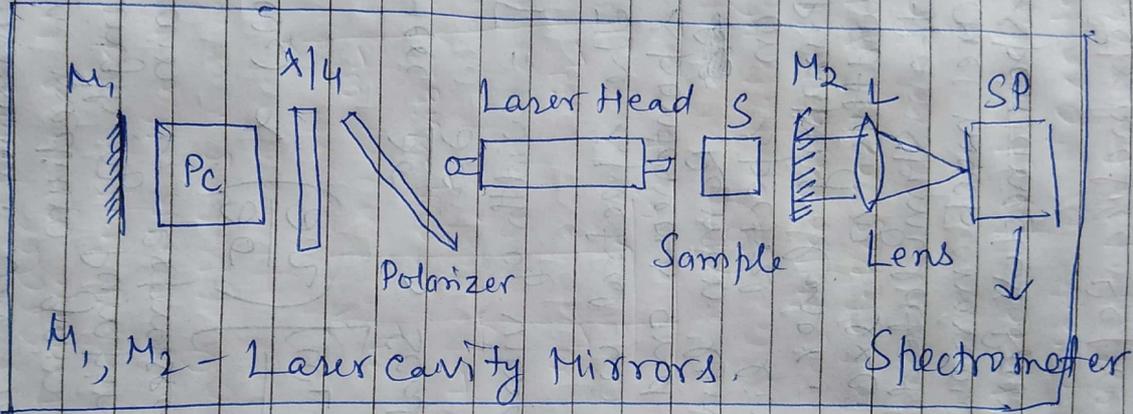
M_1, M_2 — Laser cavity Mirrors.   Spectrometer

$\dfrac{\lambda}{4} \rightarrow$ Quarter wave plate

Pc $\rightarrow$ Pockelscells.

Applications of Stimulated Raman Scattering

(1) Study of molecular conformational structures

(2) Material Composition Analysis

(3) Non-invasive label free imaging for living tissues.

(4) Ultrafast Microscopy.

Hyper Raman effect:-

In Raman scattering when more intense light is employed, non linear Raman processes occur in the sample such as hyper Raman scattering. When the intensity of incident radiation increases the probability also increases that two or three photon will participate in Raman and Rayleigh scattering. Such phenomena is called Hyper Raman scattering. The Hyper

Raman effect arises due to second order polarisability term. Figure shows Hyper Raman and Hyper Rayleigh Scattering with the involvement of two photons.
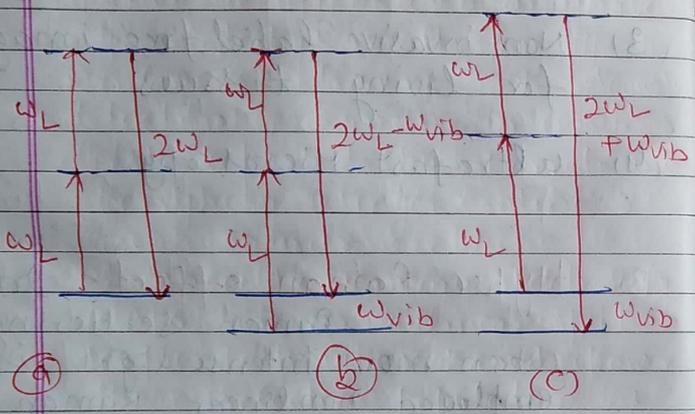
(a) Hyper Rayleigh

(b) Hyper Raman Stokes Scatt.

(c) Hyper Raman Anti-Stokes Scattering

It is a three photon process, the system is excited with two photons (ω_L) and emits one photon at the frequency $2\omega_L \pm \omega_{vib}$.

Hyper Raman spectroscopy is a modified version of Raman spectroscopy and many of basic operations are same. The signal produced by hyper Raman scattering is weak, however it can be used to provide vibrational information on some silent modes which are suppressed by conventional Raman Scattering because of issues with molecular symmetry. It is of two type

(1) Resonance Hyper Raman Spectroscopy

(2) Surface Enhancement through Plasmons

Terhune found that when a beam of giant pulse Ruby laser at $\nu_0 = 14402\ cm^{-1}$ was brought to focus inside liquid or fused quartz, a fraction of incident energy emerged as scattered radiation around $28804\ cm^{-1}$. The scattered radiation was found to vary as square of laser intensity

Photo Acoustic Raman Spectroscopy (PARS) :— In the various methods of nonlinear Raman Spectroscopy stimulated Raman spectroscopy (SRS) and coherent Antistokes Raman Spectroscopy (CARS) are often used and have given many results on the Raman spectra of gases. Acoustic detection of Raman process was first reported by Barret and Berry by using continous wave laser source.

Photoacoustic Raman Spectroscopy (PARS) is a nonlinear spectroscopic technique based upon the selective population of a system by process of Stimulated Raman scattering. The necessary condition for this process are

(1) The transistion involving the initial and final energy levels must be Raman active.

(2) It means the transistions must involve a change in the molecular polarisability.

3. The frequency difference of two incident laser beams must be adjusted to equal the frequency of this Raman active transistions.

The occurence of Raman spectrum depends on change in polarizability of molecules and not depends on transistion dipole moment. Raman active transistions can occur for only molecules that have no infra red (IR) spectrum. The PARS technique was first demonstrated experimentally using low power continous wave laser source excitation of gaseous sample. It is also used to study pure rotational Raman transistion in gases. The photo acoustic techniques are based upon direct absorption of light in the sample but PARS technique is fundamentally different because of light is not absorbed by the sample. The upper energy level of transistion is populated by

Stimulated Raman process rather than by direct absorption. The experimental arrangement for PARS is same as that required for non linear Raman techniques such as CARS and Raman Induced Kerr Effect Spectroscopy (RIKES) and Stimulated Raman gain Spectroscopy (SRGS). These techniques measure an optical signal by means of photo detector but PARS employs a microphone to sense the energy that is deposited in the sample after the passage of laser Beams.
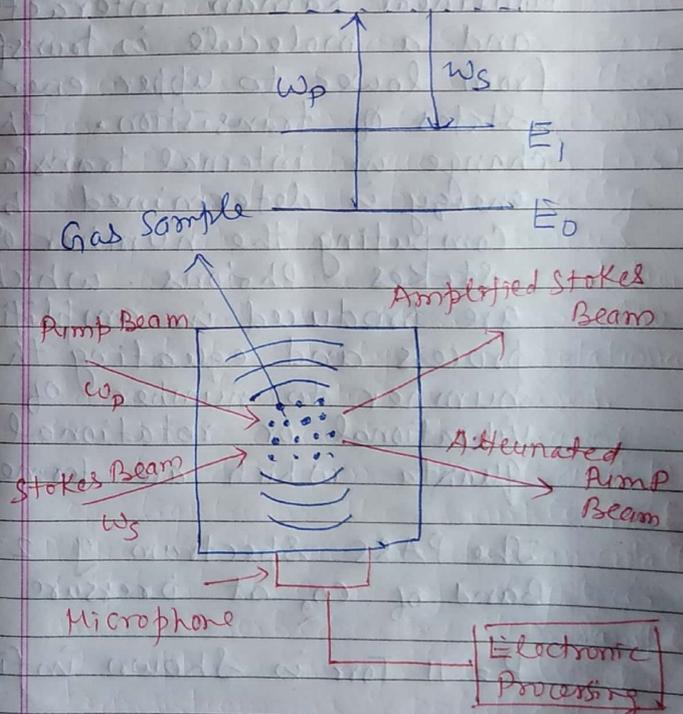
The basic features of PARS process are shown in figure. Two incident laser Beams with frequencies ω_p and ω_s interact with two energy levels E_0 and E_1 of molecule. In these frequencies ω_p is refered as pumping frequency while ω_s is refered as stokes frequency.

The Raman transistion frequency in (wavenumbers) is

$$\omega_0 = \frac{E_1 - E_0}{hc}$$

The frequency of laser is so adjusted that

$$\omega_p - \omega_s = \omega_0$$

Gas Sample

Pump Beam ω_p

Stokes Beam ω_s

Amplified Stokes Beam

Attenuated Pump Beam

Microphone

Electronic Processing

The photo acoustic Raman signal magnitude may be deduced from change in internal translational energy of sample due to stokes amplification process. one Pump photon is annihilated for every stokes photon which is generated by Nonlinear Raman interaction and a molecule is transferred from lower to upper energy states of transistion. The change in internal translation energy is determined by computing the number of stokes photons which are produced in amplification process and equating this number to number of vibrational or rotational quanta which are formed.

The PARS spectrum of $2\nu_2$ Band of CO_2 at pressure

$P = 11$ Torr is shown in figure.

/2053   Wave Number   /2861 cm^{-1}
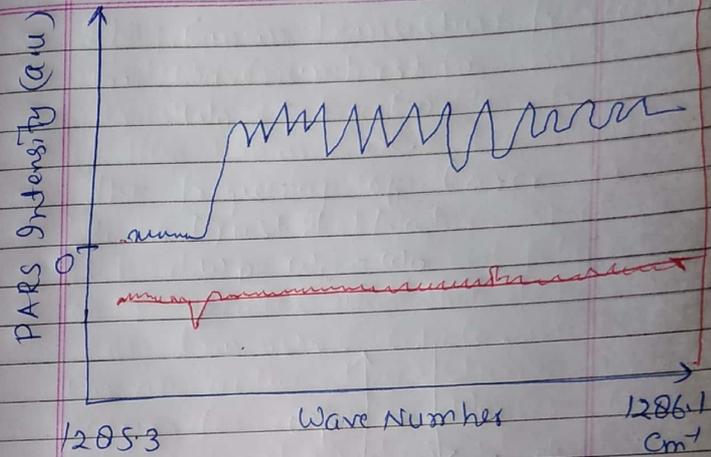
At $T = 297K$, Pumping Power
$= 400 KW$ $P_s = 100 KW$

—   → Calculated Spectra

—   → experimental Spectra

Applications of PARS:-

(1) Easy to Handle from the view of optics just mixing and focussing of two laser beams near a microphone.

(2) It provides useful information about the Raman Spectra of gases.